Counter-ion release and electrostatic adsorption

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Abstract

The effective charge of a rigid polyelectrolyte (PE) approaching an oppositely charged surface is studied. The cases of a weak (annealed) and strongly charged PE with condensed counterions (such as DNA) are discussed. In the most interesting case of the adsorption onto a substrate of low dielectric constant (such as a lipid membrane or a mica sheet) the condensed counterions *are not always* released as the PE approaches the substrate, because of the major importance of the image charge effect. For the adsorption onto a surface with freely moving charges, the image charge effect becomes less important and full release is often expected.

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A deep understanding of the adsorption of DNA or other charged biomolecules onto oppositely charged membranes is of fundamental importance to understand many key physiological processes, and many experimental studies have approached this problem from very different viewpoints [1], strongly motivated by applications to gene therapy [2]. On the theoretical side, the adsorption and the interaction of charged rods on a charged surface have been studied within the Debye-Huckel approximation in different situations [3]. In this work, we want to focus on the effective charge of the adsorbed macromolecule. We calculate the attraction energy between an infinitely long, charged cylinder (rigid polyelectrolyte or PE) parallel to an oppositely charged plane, as a function of their distance h. The energy variation leads to the determination of the equilibrium charge density of the rod as a function of h. This (effective) charge density can be interpreted in terms of the release of condensed counterions for highly charged PE such as DNA, which are beyond the Manning condensation threshold, or in terms of the recombination of ionized charges on the rod for weak (annealed) PE. We show that in contrast to what would be naively expected, the full release of the counterions condensed onto an highly charged rod is not always observed in the vicinity of an oppositely charged surface.

The adsorption energy is derived by perturbating the Gouy-Chapmann solution of the Poisson-Boltzmann equation in a planar geometry. The perturbative treatment is strictly speaking valid only for low linear charge densities τ of the rod $l_B\tau \ll 1$, where l_B is the Bjerrum length $l_B = e^2/(4\pi\epsilon)$ (all energies are in k_BT units). However, the physical picture which emerges from this calculation leads to qualitative statements concerning highly charged PE as well. We discuss the adsorption free energy on a substrate of low dielectric constant with respect to water ($\epsilon_w = 80$), which is of most practical importance in biology related problem (adsorption of DNA on a lipid membrane for which $\epsilon_{lp} \simeq 2$ [4]) and other situations (adsorption onto the mica surfaces of an SFA: $\epsilon_{mc} \simeq 6$ [5]). We have checked that the case of a membrane of thickness $l = 50A$ and dielectric constant $\epsilon_{lp} = 2$ does not show quantitative differences with the present situation ($l = \infty$ and $\epsilon_{lp} = 0$). Finally, we also study the case where the charges on the plane are free to adjust to the field created by the rod, a situation of great interest for fluid interfaces such as biological lipid membranes.

The electrostatic potential $\phi^{(0)}$ near a charged wall of density $\sigma > 0$ (or equivalently with a Gouy-Chapmann length $\lambda \equiv 1/(2\pi l_B\sigma)$), in a salt solution of average concentration n_0 (or Debye length κ^{-1} with $\kappa^2 \equiv 8\pi l_B n_0$) satisfies the Poisson-Boltzmann (PB) equation [6]. In the low salt limit $\kappa\lambda \ll 1$, which is the case discussed in this paper, the potential near the wall ($\kappa z \ll 1$) follows the Gouy-Chapmann (G-C) law [7]:

$$\phi^{(0)} = 2\log\frac{\kappa(\lambda + z)}{2} \quad n^{(0)}(z) = \frac{1}{2\pi l_B(\lambda + z)^2} \tag{1}$$

where z is the coordinate normal to the wall ($z = 0$ at the interface), $n^{(0)}$ is the density of (negative) counterions (or c-i) near the wall. The Gouy-Chapmann solution predicts a dense counterion layer (the G-C layer) of thickness λ containing a finite fraction of the c-i, followed by a diffuse c-i region. The local screening length in the G-C layer is small: $L_\kappa \simeq \lambda/\sqrt{2}$, while the screening length of the diffuse region is self-similar: $L_\kappa \simeq z/\sqrt{2}$. For distances larger than the Debye length: $z > \kappa^{-1}$, the electrostatic potential decreases exponentially.

The potential variation $\delta\phi$ due to a negatively charge rod (of linear charge density $-\tau$) located at an altitude $z = h$ above the plane is calculated by a linear expansion of the G-C

theory, provided that the perturbation is small. A small perturbation of Eq.(1): $\delta n \ll n^{(0)}$ (note that δn is an algebraic average taking into account the sign of the free charges) supposes that the perturbation potential $\delta\phi$ is smaller than unity. The calculation of the potential is carried out in Fourier space for the coordinate x parallel to the wall and perpendicular to the rod: $\tilde{f}_q = \int dx e^{iqx} f(x)$. The linearized PB equation and the boundary conditions are:

$$\partial_z^2 \delta\tilde{\phi} = \left(q^2 + \frac{2}{(z+\lambda)^2}\right)\delta\tilde{\phi} \qquad \partial_z\delta\tilde{\phi}|_{z=0} = 0$$
$$\text{and} \quad \partial_z\delta\tilde{\phi}|_{z=h_+} - \partial_z\delta\tilde{\phi}|_{z=h_-} = 4\pi l_B \tau \tag{2}$$

with natural boundary conditions for $z \to \infty$

From the perturbed potential $\delta\phi(x,z)$, the free energy due to the presence of the rod can be calculated by a charging process of the rod: $\delta\mathcal{F} = \int_0^\tau \left(\phi_{z=h}^{(0)} + \delta\phi_{z=h}\right) d\tau$. The first part of the integral gives the interaction energy between the rod and the charged plane and the unperturbed G-C counterion layer, while the second part represents the self-energy of the rod, and its interaction with the perturbed c-i cloud. The direct interaction energy is:

$$\delta\mathcal{F}_{int} = 2\tau \log \frac{\kappa(\lambda+h)}{2} \tag{3}$$

The solution of the perturbed PB equation Eq.(2) leads to the "self-energy": $\delta\mathcal{F}_{self} = 1/2 l_B \tau^2 \mathcal{I}_p$, with

$$\mathcal{I}_p = \int_0^{p_M} dp \frac{\left(1+p(1+\bar{h})\right)^2}{p^3(1+\bar{h})^2} \times$$
$$\left(e^{-2p\bar{h}}\frac{1-p+p^2}{1+p+p^2} - \frac{1-p(1+\bar{h})}{1+p(1+\bar{h})}\right) \tag{4}$$

with $p \equiv q\lambda$ and $\bar{h} \equiv h/\lambda$. The integral cutoff is $p_M \equiv 2\pi\lambda/a$ where a is a "microscopic" size of order the rod radius ($a = 20A$ for DNA [8]). This complicated expression can be approximated in the two important limits: for $h \gg \lambda$

$$\delta\mathcal{F}_{self} \simeq \frac{1}{2} l_B \tau^2 \left(\frac{2}{3} + \log\left(\frac{4\pi}{3}\frac{h}{a}\right)\right) \tag{5}$$

and for $h \ll \lambda$.

$$\delta\mathcal{F}_{self} \simeq \frac{1}{2} l_B \tau^2 \left(-\Gamma + \frac{2\pi}{3\sqrt{3}} + \log\frac{\pi\lambda^2}{ah}\right) \tag{6}$$

The self-energy behaves very differently for large and small distances from the wall. It shows an attraction between the rod and the plane at large distances (the energy increases with the distance), which superimposes to the bare attraction between the two oppositely charged macroions. At short distances, there is a strong (logarithmically divergent) repulsion between the rod and the plane (Eq.(6)).

The self-energy shows a deep minimum for a position of the rod which only depends upon the G-C length: $h_{min} \simeq 0.8\lambda$. This minimum results from a balance between the repulsive

image charge effect and the attraction due to the screening of the c-i in the Gouy-Chapman layer. The self-energy of a cylinder in a bath of mobile charges is of order $l_B \tau^2 \log L_\kappa/a$, where L_κ is the characteristic ("screening") length of the bath. This energy can be interpreted as the interaction free energy of the charges on the cylinder (the interaction having a range L_κ). Note that although the free ions are mostly of the same sign as the rod, one can speak of a "screening" effect, as the interaction between the rod and the unperturbed ion cloud is taken into account in $\delta\mathcal{F}_{int}$ (Eq.(3)). In addition to the self-interaction, one should consider the interaction with the image charge, which in the case $\epsilon_{z<0} \ll \epsilon_{z>0}$, is a virtual rod of same charge located at $z = -h$ [9]. This gives an extra contribution $\sim l_B \tau^2 \log L_\kappa/h$ per unit length. The large and short distance behaviors Eq.(5,6) can now be explained from the counterion profile Eq.(1), since $L_\kappa \sim h$ for $h > \lambda$ and $L_\kappa \sim \lambda$ for for $h < \lambda$.

The adsorption of a polyelectrolyte onto a biomembrane or other fluid membranes, which are generally a mixture of charged and neutral lipid molecules, involves the movement of surface charges as a response to the field created by the rod. We address this case, disregarding the fact that the lipid bilayer is a flexible object which would, to a certain extent, wrap around the PE [10] - this interesting phenomenon will be studied in future works. We also assume that the charge reorganization at the interface is not limited by the availability of moving charges on the plane. The charge on the plane follows a Boltzmann law: $\sigma = \sigma_0 e^{-\delta\phi}$. As a result, the boundary condition for the perturbed field on the plane (corresponding to Eq.(2)) has to be modified: $\partial_z \delta\tilde{\phi}|_{z=0} = 4\pi l_B \sigma_0 \delta\tilde{\phi}|_{z=0}$. This affects the self-energy term only, which can be expressed similarly to Eq.(4): $\delta\mathcal{F}_{self} = 1/2 l_B \tau^2 \mathcal{I}_p^{bis}$ with

$$
\mathcal{I}_p^{bis} = \int_0^{p_M} dp \frac{\left(1 + p(1 + \bar{h})\right)^2}{p^3(1 + \bar{h})^2} \times
$$
$$
\left(e^{-2p\bar{h}} \frac{3 - 3p + p^2}{3 + 3p + p^2} - \frac{1 - p(1 + \bar{h})}{1 + p(1 + \bar{h})} \right) \tag{7}
$$

For $\bar{h} > 1$ this self-energy is equivalent to the constant surface charge case (Eq.(5)), while for $\bar{h} < 1$, the approximation gives:

$$
\delta\mathcal{F}_{self} \simeq \frac{1}{2} l_B \tau^2 \left(-\Gamma - \frac{\pi}{3\sqrt{3}} + \log \frac{\pi\lambda^2}{6ah} \right) \tag{8}
$$

The mobile (positive) charges of the surface are attracted toward the rod ($x = 0$); this effectively decreases the "Gouy-Chapman" screening length around the PE and reduces the image charge effect. The case of an annealed surface charge is qualitatively similar to (see scaling in Eq.(8)), but quantitatively different from the case of a quenched surface charge. Since the repulsion of the wall is weakened, the minimum of the self-energy is much deeper, and closer to the wall in the case of moving surface charges.

We now discuss the variation of the line charge of an annealed, or weak, polyelectrolyte near a charged wall. The charges on the chain result from a partial ionization of specific chemical groups. The ionization occurs at chemical equilibrium with the free ions in solution, and is governed by quantities such as the pH of the solution [11]. Formally, the PE charge density can be determined by equating the chemical potential of the charges on the chain, to a (given) chemical potential μ_0 for the free charges. For an infinitely long rigid PE in a salt solution, the free energy (per unit length) of the charges on the chain is the sum

of the translational entropy of the charges along the rod, the electrostatic energy, and the chemical potential: $\mathcal{F} = \tau \log \tau a/e + l_B \tau^2 \log \kappa a - \mu_0 \tau$. The equilibrium charge density of the rod for a given chemical potential is obtained by differentiation of the free energy: $\mu_0 = \log \tau a + 2 l_B \tau \log \kappa a$. The equivalent expression for a charged rod near an oppositely charged plane can be computed from the electrostatic free energy Eq.(3,4): $\mu_0 = \log \tau a + 2\pi l_B \tau \ \mathcal{I}_p + 2 \log \kappa(\lambda + h)/2$. Because of the minimum in the self-energy, the equilibrium charge density τ is maximum for a finite height of order the G-C length, and decreases sharply near the wall. This non-trivial behavior of the charge density of an annealed PE near a wall is mostly due to the importance of the image charge effect in the vicinity of the wall. It is extended further below in the case of highly charge PE with Manning condensation. Note that the optimum charge of the weak PE can reach higher values if the charges on the surfaces are mobile, but still decreases at shorter distances.

The perturbative treatment is expected to fail in the important case of the release of the counterions condensed onto a highly charged rod, as the rod approaches an oppositely charged plane. However, the qualitative argument which translates the concentration of free charges into a local screening length should still hold in this case.

A charged cylinder surrounded by its counterions undergoes the so-called Manning condensation [12]. Solutions of the poisson-Boltzmann equation in this geometry [13] predict that if the rod is highly charged (namely $l_B \tau > 1$), a finite fraction $1 - \beta$ of the counterions are confined in the close vicinity of the rod. The electrostatic properties at large distances from the rod are the same as those of a rod with an effective charge $l_B \tau^* \simeq 1$. The (over)simplified Oosawa picture of counterion condensation [14] gives a qualitative account of this phenomenon [15]; it is based on a chemical equilibrium between two types of counterions: condensed c-i with a reduced entropy and subjected to a large electrostatic attraction from the rod on the one hand, and free c-i in solution far from the rod on the other hand. This picture can be adapted to the case of a cylinder of charge τ in a salt solution of density n_0 (or screening length κ^{-1}). The effective charge of the cylinder, $\tau^* = \beta\tau$, is obtained by balancing the chemical potentials of the condensed c-i $\mu_{cond} = \log \left[\frac{(1-\beta)\tau v}{\pi a^2} \right] + 2 l_B \tau \beta \log [\kappa a]$ and of the c-i dispersed among the salt molecules $\mu_{free} = \log [n_0 v]$ (v is the volume of a c-i molecule). The resulting fraction of free c-i β is: $\log [8 l_B \tau (1 - \beta)] = (1 - l_B \tau \beta) \log [(\kappa a)^2]$. This result is very similar to the Oosawa relationship for a rod which would occupy a (small) volume fraction $\Phi = (\kappa a)^2$ in a salt-free solution [16], namely $\beta \simeq 1$ for $l_B \tau < 1$ and $\beta l_B \tau \simeq 1$ for $l_B \tau > 1$.

The counterion condensation on a rod near a charged plane can be derived in the same way. The chemical potential of the condensed counterions depends upon the electrostatic potential on the rod, which can be determined (at the level of the scaling laws) using the calculation of the previous sections. Equating the chemical potentials of the free and condensed c-i, we obtain the fraction of free c-i β:

$$\log [8 l_B \tau (1 - \beta)] = \log \left[(\kappa a)^2 \right] -$$
$$2 l_B \tau \beta \log \left[\frac{ah}{L_\kappa(h)^2} \right] + 2 \log \left[\frac{\kappa(h + \lambda)}{2} \right] \tag{9}$$

where the local screening length follows the asymptotic behaviors: $L_\kappa = \lambda$ for $0 < h < \lambda$ and $L_\kappa = h$ for $\lambda < h < \kappa^{-1}$. Examples of the counterion release as a function of the distance to the wall is shown on Fig.1 (for which proper screening due to the salt has been taken

into account for $\kappa h > 1$). The Manning parameter $l_B \tau = 4$ and the radius $a = 20A$ are of order those for DNA, three surface charge densities ranging from $\lambda = 200A$ to $50A$ as been considered, corresponding to one charge every $(100A)^2$ to $(50A)^2$. The salt concentration $\kappa^{-1} = 1000A$ corresponds to a concentration of $10^{-5} mol/l$. While the c-i are released as the rod penetrates the Gouy-Chapmann layer, full release ($\beta = 1$) is only reached for $\lambda = 50A$ - the maximum being 60% for $\lambda = 200A$ (it is of the order of 30% for the free rod). Furthermore, the free charges recondense at short distance if λ is large enough; the effective charge reaches 50% of the bare charge for $\lambda = 200A$. It can be shown that for large salt concentration or weak surface charge of the wall: $\kappa^2 \lambda^3 < 2a$, the PE in contact with the wall can have a lower effective charge than the free PE.

It should be noted that the short range repulsion due to the image charge can prevent real adsorption with an equilibrium contact between the rod and the plane. In many cases, however, a short range attraction of non electrostatic origin (such as a hydrophobic force) dominates the adsorption. This interaction must be added to the electrostatic free energy calculated here in order to study the equilibrium adsorption.

Different conclusions are reached in the case of moving surface charges. A highly charge rod has a strong effect on the surface charge distribution, for the potential it creates is likely to dominate over the Gouy-Chapman potential, even near the wall. A quantitative description of the phenomenon would require the solution of the full non-linear Poisson-Boltzmann equation, with complex (non-linear as well) boundary conditions. In the following, we merely try to give a feeling of the way moving charges can influence the counterion release of an adsorbed polyelectrolyte. We assume that the surface charge distribution obeys Boltzmann statistics: $\sigma_{x=0} = \sigma_0 e^{-\phi_h}$, where the potential ϕ_h created by the rod at the surface reflects the screening due to the Gouy-Chapmann layer, the image charge, and the fraction $(1 - \beta)$ of condensed counterions: $\phi_h \sim -2l_B \tau \beta \log (L_\kappa/h)^2$. Since the local screening length $L_\kappa \simeq (\lambda + h)/\sqrt{2}$ is influenced by the surface charge σ, which in turn, depends upon the screening length, we obtain a self-consistent relationship for the local Gouy-Chapman length near the rod:

$$\lambda(h) \left(\frac{h + \lambda(h)}{\sqrt{2}h} \right)^{4l_B \tau \beta} = \lambda_0 \tag{10}$$

This expression shows that moving surface charges strongly reduce the screening length near the rod, which becomes of order h when the rod is close to the wall (recall that $l_B \tau \beta \simeq 1$). As a consequence, the interaction with the image charge and the self-interaction along the rod are both strongly screened. The dominant interaction between the cylinder and the wall is the attractive part given by Eq.(3), and we are likely to observe a full release of the condensed counterions in this case.

To summarize, we have studied the evolution of the effective charge of a polyelectrolyte near an oppositely charged plane. The case of a weak PE is studied fairly rigorously, via a perturbative treatment of the non-linear Poisson-Boltzmann equation. We show that at large distance, the charge of the PE increases as the distance to the wall h decreases, as expected. However, the charge decreases "strongly" as the PE enters the Gouy-Chapman layer ($h \simeq \lambda$) because of the combined effect of image charge (for the most common case of a wall with a low dielectric constant) and self-interaction along the PE. These two effects are very much influenced by the value of the Gouy-Chapman length λ, and are partly suppressed in the

case of a fluid interface with moving surface charges (for a fluid lipid bilayer for instance), where the charge of the adsorbed PE can reach higher values.

The most interesting case of a strongly charge PE beyond the Manning condensation threshold (such as DNA) is discussed qualitatively, using "scaling" arguments inferred from the perturbation theory. We predict that in the case of fixed surface charges, and in contrary to a widely spread idea, most of the condensed counterions <u>are not released</u> if the Gouy-Chapman length is larger than the radius of the rod: $\lambda \gg a$. In the case of freely moving surface charges, a full release of the condensed counterions is expected, as the effective Gouy-Chapman length near the rod is of order the rod radius.

In all the discussion, we have assumed that the Gouy Chapman length is larger than a molecular size. In many real cases, the two lengths are of the same order of magnitude and the finite size of the ions must be taken into account in order to obtain quantitative results. In this case our results can at best be considered as qualitative.

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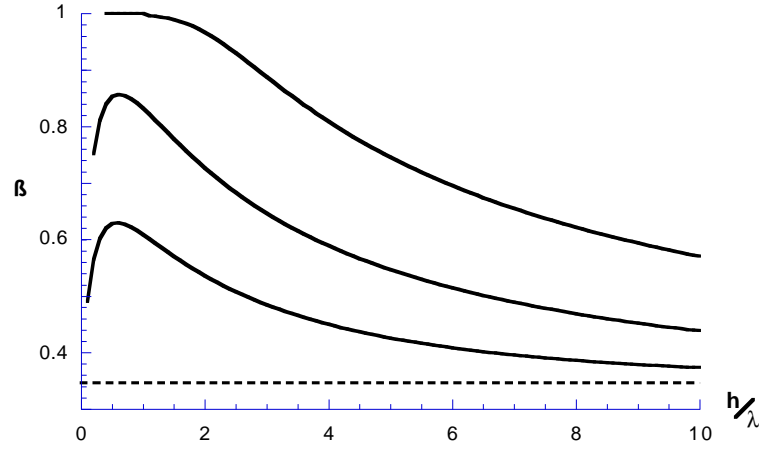[16] The relationship is $\log \frac{1-\beta}{\beta} = (1 - l_B \tau \beta) \log \Phi$

FIG. 1. Fig.1 Fraction β of free counterions as a function of the distance to the wall in λ units (dashed: $\beta(h \to \infty)$) for $a = 20A$, $l_B\tau = 4$, $\kappa^{-1} = 1000A$, for decreasing values of the Gouy-Chapmann length: $\lambda = 200A$, $100A$ and $50A$